

Lead transfer in the soil-root-plant system in a high contaminated Andean area

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Soil lead is not an essential factor in agricultural production; on the contrary, it is a heavy metal that is highly toxic to the nutritional food system. This study was conducted in 2018 to evaluate the level of lead transfer and bioaccumulation in the soil-root-plant system in high Andean grasslands in a geographic area near La Oroya, in the central Andes of Peru, where large companies have been engaged in mining-metallurgical activities for almost a century, contaminating the air, water, soil and grasslands, reducing the quality of the soil and food and causing damage to the environment and human health. In this context, lead levels were measured in 120 samples of topsoil (0-20 cm), root and shoot of high Andean grasslands in a systematic study, and lead concentrations were determined by the method of flame atomic absorption spectroscopy. No significant differences between soil pH, organic matter content and lead were found among the samples evaluated ($P > 0.05$). Mean Pb concentrations decreased in the order soil > root > shoot ($P < 0.01$). Pb levels in soil, root and shoot of high Andean grasses were 212.36 ± 38.40 , 154.65 ± 52.85 and 19.71 ± 2.81 mg / kg. Pb transfer factors from soil, roots and shoots were 0.74 ± 0.26 and 0.14 ± 0.06 , and Pb bioaccumulation factors from soil, roots and shoots were 0.10 ± 0.03 . Average soil and shoot lead concentrations exceeded the maximum limits of international regulations. Lead in soil was 3.4 times higher than the maximum limit for agricultural soil and in forage was 1.97 times higher than the limit value for this foodstuff. Our findings are important and shocking and show that pastures in the Andean areas of Peru would have high levels of Pb compared to other regions and the world, which could cause socio-economic and health problems in exposed populations.

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Abstract

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Subjects: Environmental Contamination and Soil Science, Ecosystem Science, Environmental impacts

Keywords: Heavy metals, Contaminated soil, Soil pH, Forage quality, Lead bioaccumulation, Smelting, Bioaccumulation factor, Lead in plants, Highland Andes Peru.

Introduction

Lead (Pb) is a toxic metal (11.4 g / cm^3) naturally present in the earth's crust in harmless concentrations, usually between 15 and 40 mg / kg (Assi et al., 2016), but is the second most dangerous substance (Fahr et al., 2013). Due to its multiple uses, it is widely used in industry (Wuana & Okieimen, 2011) and in its metallurgical process it produces fine particulate material that travels many kilometers through the air (Suvarapu & Baek, 2017; Martin et al., 2017) and when it exceeds certain limits it geoaccumulates, bioaccumulates and biomagnifies (Lokeshwari & Chandrappa, 2006). It is deposited in water and soil and transferred to plants, animals and humans (Li et al., 2017) reaching toxic levels with serious consequences for ecosystems (Alloway, 2013; Kong, 2014), with adverse effects on plants, animals and humans, especially

babies and children (Kryshna & Mohan, 2016; Chirinos-Peinado & Castro-Bedriñana, 2020). It contaminates groundwater and reduces the quality of soil and food (Martin et al., 2017).

Anthropogenic Pb released into the atmosphere is deposited and accumulates in the upper soil layer (Bacon, Hewitt & Cooper, 2005), and because of its long biological half-life and high bioaccumulation potential, it is absorbed by grass roots (Nascimento et al., 2014; Hou et al., 2014), generating unsafe Pb-laden foods that harm human health (Li et al., 2005; Castro, Chirinos & Rios, 2016).

Soil quality plays an important role in food security by determining the possible composition of forage at the early levels of the food chain (Tóth et al., 2016); therefore, top soil analysis (typically the upper 0-20 cm) is valuable for assessing heavy metal contamination in grasslands (Ekengele, Danala & Zo'o, 2016; Martín et al., 2017).

Soil contamination and its potential impact on human health has not been studied extensively in Peru, especially in the high Andean areas, where mining and metallurgical activities are carried out in addition to livestock activities. Elsewhere, such as in Europe, 93.76 per cent of its agricultural land has been found to be safe for food production and only 137,000 km² (6.24 per cent) is estimated to be contaminated by heavy metals and needs to be assessed locally and remedial action taken (Tóth et al., 2016); such information is not available in Peru.

Although mining generates the largest percentage of net exports and foreign exchange to Peru, the central highlands may have marked accumulations of Pb in surface soils that are transferred to pastures and other crops. The polymetallic mining-metallurgical center located in the central sierra, which has been in operation since 1992, generated uncontrolled emissions between the 1970s and 1990s, and although some processes were subsequently optimized, reducing Pb emissions to the air, emissions of particulate matter and acid fumes continue to exceed international standards and contaminate the surrounding ecosystems (Álvarez-Berrios et al., 2016). La Oroya is the fifth most contaminated place on the planet (Blacksmith Institute, 2007) and in these almost 100 years, the vegetation and soil of the central region of Peru have been contaminated by a series of heavy metals and toxic substances (Alvarez-Berrios et al., 2016; USDA, 2017).

A recent study shows that the milk produced in an area close to the metallurgical industry presents quantities of Pb and Cd higher than the maximum permitted levels (Chirinos-Peinado & Castro-Bedriñana, 2020), which makes soil quality an issue of economic and social importance (Kong, 2014) not only for Peru, but for the world.

There is great interest in studying the bioaccumulation of heavy metals in forages, since they are the basis of the food chain. From this point of view, our study addresses the bioaccumulation of Pb in high Andean pastures in highly contaminated soils in an area near the city of La Oroya.

We evaluated the topsoil, roots and shoots of natural and cultivated pastures in a livestock area between April and September 2018. This study expands our knowledge of the dynamics of Pb transfer in the soil-root-sprout system under highly contaminated conditions.

In general, the knowledge of contaminant levels in food is generated in controlled studies, with pre-set amounts of samples in controlled environments during a limited period (Adamse,

Van der Fels-Klerx, de Jong, 2017). A strength of our ecological study is that it allows us to study the problem over time and provides information on the levels of lead in grasslands to establish monitoring priorities and continue research on the dynamics of lead in the soil.

Materials and methods

Ethical approval

The study protocol was approved by a group of experts appointed by the University General Research Institute. The institutional authority of the high Andean community where the research was conducted approved the field study and the soil and pasture sampling.

Description of the study site

The research was carried out in the pastures of the Pacha Peasant Community, located in the central Andes of Peru, department of Junin, province of Yauli (11°32'10" South Latitude and 75°45'20" West Longitude, average altitude 3750 m, minimum and maximum temperature of - 3.1 and 18.2°C), covering 16,564 ha of pastures, of which 13.73 ha are irrigated.

The study site is located 20 km from the La Oroya Polymetallic Metallurgical Complex, which has been in operation since 1922. Figure 1 shows the location map and the distribution of soil, root and shoot sampling points of cultivated and natural pastures in the two collection periods.

This area was chosen because it is representative of the communities near the fifth most contaminated city on the planet (Blacksmith Institute, 2007), which due to their agro-ecological conditions are dedicated to raising cattle, sheep and alpacas.

In the area of study, the cattle have approximately 11 ha (hectares) of natural pasture, with the following species standing out: *Festuca dolichophylla*, *Bromus catharticus*, *Bromus lanatus*, *Nasella meyeniana*, *Calamagrostis heterophylla*, *Piptochaetium faetertonei* *Nasella publiflora*, *Asiachnae pulvinata*, *Margaricarpus pinnatus*, *Oenothera multicaulis*, *Trifolium amabile* and small extensions of associated grasses (6 ha) *Lolium perenne* and *Trifolium repens*, installed 15 years ago and currently have a poor condition.

The quantification of Pb in soil, roots and shoots of the high Andean grasses was carried out in the SAC laboratory of Baltic Control, accredited by the National Institute of Quality of Peru.

Figure 1. Partial map of La Oroya-Peru, research area (3900-4500 m altitude).

The image above shows the path from La Oroya Mining-Metallurgical complex.

The lower image shows the study site and distribution of sampling points (1 m²/sample).

Communal stable: to 20 km from La Oroya City.

■ Sampling area (n = 10) of pastures cultivated - April samples

■ Sampling area (n = 10) of pastures cultivated - September samples

○ Sampling area (n = 10) of natural pastures - April samples

● Sampling area (n = 10) of natural pastures - September samples

Sampling procedures

Considering that most crop roots are present in the upper 20 cm of the soil (Evans, 1978), topsoil sampling (0-20 cm) was carried out at 20 points in the natural grassland area and 20 points in the cultivated grassland area (Figure 1), which were collected in April and September 2018. A total of 120 samples were collected using standardized sampling procedures (Tóth et al., 2016; Li et al., 2016; Martin et al., 2017; Castro-Bedriñana, Chirinos-Peinado, Peñaloza-Fernández, 2020). Soil and grasses of 1 m² were sampled with a stainless-steel shovel, taking approximately 0.5 kg of soil from each and the grasses present (Tóth, Jones, Montanarella, 2013).

The soil and grass samples are from the same sampling site (Figure 1). The grasses were divided into root and aerial parts (García-Gallegos et al., 2011; Castro-Bedriñana, Chirinos-Peinado, Peñaloza-Fernández, 2020). All samples were placed in first-use polyethylene bags with zippered closure to be taken to the laboratory.

Laboratory analysis

The soil samples were dried at normal temperature, pulverized and sieved on a 100-mesh screen, obtaining a fine and homogeneous powder. The samples were digested using the USEPA 3050B method (SW-846). Roots and shoots were washed with running water and rinsed with deionized water, dried and ground for analysis.

Repeated additions of a mixture of concentrated nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) were made to one gram of dry sample. Hydrochloric acid (HCl) was added to the initial digestate and the sample was refluxed. The digestate was diluted to a final volume of 100 ml (USEPA, 1996).

To quantify the Pb concentration of the different samples, the standard analysis procedure was followed (Tóth, Jones, Montanarella, 2013), using flame atomic absorption spectroscopy (FLAA), based on the protocol of the AOAC Official Method 975.03 (AOAC, 1990; USEPA, 1996). To ensure analytical precision, the blank method, duplicate samples, and the high- and low-range control standard were used for every 15 samples analyzed. For the calibration curve, Sigma-Aldrich Pb standard 986 ± 4 mg / kg was used. The detection limit for Pb was 0.2 mg/kg. The units of concentration of Pb were expressed in mg/kg.

To assess the Pb concentration in soil, the international threshold of 60 mg/kg was used (MEF, 2007) and for forage, the maximum Pb limit was 10 mg/kg dry matter, considering that limits in the normal plant range from 0.5 to 10 mg / kg dry matter (Kabata-Pendias & Pendias, 2001; Boularbah et al., 2006).

Lead transfer factor and bioaccumulation

The transfer factor (TF) represents the potential transmission capacity of heavy metals from the soil to different parts of a plant (Hu et al., 2017). The equations used to estimate the TF of Pb from soil to root (TF_{sr}), from root to shoot (TF_{rs}) and the bioaccumulation from soil to shoot (TB_{ss}) were the following:

$$TF_{sr} = [Pb\ root]/[Pb\ soil]$$

$$TFrs = [Pb\ Shoot]/[Pb\ Root]$$

$$TBss = [Pb\ Shoot]/[Pb\ soil]$$

Statistical analysis

To compare the Pb content between soil, root, and shoot samples from natural and cultivated pastures per sampling period, analyses of variance and Tukey tests were performed with a significance level of 5% using SPSS 23. To compare the level of Pb in soil and grass with the maximum permissible limits, "t" tests were performed for a single sample. The values of the maximum Pb limits in soil and grass were 60 and 10 mg/kg, respectively.

Results

Soil properties and Pb content

No significant differences were found between soil pH by sampling period and by type of grass ($P > 0.05$). The pH range was between 5.03 and 7.73, with an average of 6.36, indicating that the soils evaluated are weakly acidic to neutral (Table 1).

Table 1. Average and range of pH, organic matter (OM) and Pb content in the soil in different study periods in an area near the polymetallic smelter in the central Andean region of Peru.

Lead concentration in soil, roots and shoots

Table 2 summarizes the results of average Pb concentrations in topsoil (0-20 cm), roots and shoots of high Andean pastures.

Table 2. Lead concentration in soil, roots and shoots of high Andean pastures (mg / kg) in an area near the polymetallic smelter in the central Andean region of Peru.

Figure 2. Average lead concentration in soil, roots and shoots from high Andean pastures in an area near the polymetallic smelter in the central Andean region of Peru. The maximum permissible values of Pb in soil and grass are shown (MEF 2007; Kabata-Pendias & Pendias, 2001; Boularbah et al., 2006).

Lead transfer and bioaccumulation factors

The TFsr was 0.74 ± 0.26 , with a range between 0.66-0.83 (Table 3, Figure 3); result that differs with the observations of Li et al. (2005) that reports a Pb availability in soils lower than 1%.

Table 3. Lead transfer factors in the soil-root-sprout system in high Andean pastures in an area near the polymetallic smelter in the central Andean region of Peru.

Figure 3. Lead transfer factors in soil-root-shoots system from natural and cultivated pastures in an area near the polymetallic smelter in the central Andean region of Peru.

The TBss was 0.10 ± 0.03 , with a range between 0.09-0.10, a result that shows that the root bioaccumulates the most Pb from the soil. The TFRs was 0.14 ± 0.06 , with a range between 0.12-0.16; in other words, the maximum transference percentage was 16%, leaving 84% of Pb concentrated in the root.

Discussion

Soil properties

The soils were medium to thin, loam to sandy loam (USDA, 2017), neutral to slightly acidic in pH. These edaphic characteristics are generalized in the soils of the central highlands of Peru. Unmodified or weakly modified soils are poor in nutrients and maintain their nutritional status by relying on natural biogeochemical processes (McLaughlin et al., 2000); these soils are especially sensitive to the effects of heavy metal contamination.

The OM and Pb contents in the soil were similar by type of grass and sampling period ($P > 0.05$), so the degree of solubility and bioavailability of Pb for plants would also be similar throughout the year (Lokeshwari & Chandrappa, 2006; Nas & Ali 2018), maintaining chronic contamination.

The results are indicative of the poor OM of the high Andean soils of central Peru; and, although Pb has a weak capacity to inhibit the decomposition of matter, due to its low solubility and persistent toxicity (Enya et al., 2020), improvements should be implemented so that the soil has at least 5% of OM, recommending fertilization with the manure of high Andean cattle.

Lead concentration in soil, roots and shoots

The soils of La Oroya have received contamination since the smelter industry began operations in 1922 (Chirinos-Peinado and Castro-Bedriñana, 2020). For 2007 and 2008, it reported an average concentration of $PM_{2.5}$ particles in La Oroya and a study area of 32.4 and 20.3 $\mu g / m^3$, which exceed the ECA $PM_{2.5} = 15 \mu g / m^3$ (MINAM, 2008) and 52.3 and 42.4 $\mu g / m^3$ of PM_{10} (FSS $PM_{10} = 50 \mu g / m^3$), which is deposited in the soil, then assimilated by plants and animals, affecting human health at the end of the food chain (Kryshna and Mohan, 2016; Li et al, 2017), since under similar conditions a 5% increase in mortality for every 50 $\mu g / m^3$ of Pb in the air is reported (WHO, 2006).

Pb content decreased in the order of soil > root > shoot ($P < 0.01$), which is consistent with other findings (Peláez-Peláez, Bustamante & Gómez, 2016). Lead concentrations in the soil root shoot (Figure 3) are above the maximum allowable levels, 60 mg/kg in the case of soil and 10 mg/kg in the case of shoots. The enrichment of Pb in the grass roots would act as a barrier to the translocation of heavy metals to the aerial part of the grasses.

Lead concentration in the soil

The current result is much higher than the world average (25 mg / kg) and it seems likely that Pb in the soils of the central Peruvian highlands are at the upper end on a global scale, as identified above (Castro-Bedriñana, Chirinos-Peinado, Peñaloza-Fernández, 2020).

The reference value for mean soil Pb concentrations is 60 mg / kg (MEF, 2007), and in the present study, concentrations for natural and cultivated pasture soils were 219.12 and 205.6 0.016 mg / kg. Comparing the mean Pb concentration in the soil of the study area (212.36 mg / kg) with the maximum limit for agricultural soils (MEF, 2007), it was observed that the mean Pb concentration was 3.54 times higher than the maximum limit for agricultural use and pasture production ($P < 0.01$), with implications for South American cattle, sheep and camelids and consequently for public and environmental health (Chirinos-Peinado and Castro-Bedriñana, 2020). Similarly, it was 4.35 times higher than the limit for forage cultivation recommended by Kabata-Pendias and Pendias (2001) of 50 mg Pb / kg of soil; it was also higher than other international references (Peláez-Peláez, Bustamante & Gómez, 2016) that indicate a range of 7.5 to 135 mg / kg for agricultural soils in the United States of America, and those indicated by the Peruvian Ministry of Agriculture, of 70 mg / kg (MINAM, 2017). These findings are important and shocking, and could even have legal significance, since mining-metallurgical companies would be altering environmental, animal and human health, and would also be causing damage to the economic systems that affect people exposed to these conditions.

The results of this study are also well above what was determined in the Auckland region of New Zealand, with a Pb content between 1.5 and 65 mg / kg (ARC, 2007) indicating that their soils are moderately contaminated reporting a Pb content of 11.4 mg / kg in the last 15 years (Auckland Council, 2015).

Scientific information indicates that Pb concentrations in the soil between 10 and 30 mg / kg do not affect plant growth (Mlay and Mgumia, 2010); currently, the concentrations are of high risk to human health because they are incorporated into crops grown in this lead-laden soil. Pb concentrations in soil of 100-400 mg / kg are considered toxic, and in this study the values were within this range, being toxic to plants, animals and their products, so it is recommended to monitor the impact of soil contamination on their quality and crops (Morera et al., 2013). These results serve as information to evaluate the load of Pb in the environment and its potential to enter the food chain (Hou et al., 2014), and the mining-metallurgical industry should control and reduce its emissions, which can remain in the environment for 150 to 5000 years (Saxena et al., 1999).

In Peru, the problem of contaminated soils and the products obtained from them have been neglected, which forces us to think about an integrated management of soils, which includes their evaluation, use planning, territorial ordering and decontamination strategies to apply environmental quality safety.

Lead concentration in the root

The average Pb content in the roots of natural and cultivated grasses was between 125.35 and 183.96 mg / kg. This high Pb content would force the plants to develop tolerance mechanisms in their root system, avoiding the higher Pb absorption and its retention in the vacuole, affecting the growth and branching pattern of the roots and the rate of Pb translocation to the aerial parts of the plant (Fahr et al., 2013). It was observed that the Pb transfer factor from

the root to the shoot is relatively low, a result that suggests that the root would act as a Pb accumulating organ protecting the edible part of the plant (table 2).

In this highly contaminated environment, the roots develop various mechanisms to attenuate the absorption and transfer of Pb to the aerial parts of the plant and reduce its harmful effects (Fahr et al., 2013). In some plants, there is callus formation between the plasma membrane and the cell wall that acts as a barrier against metals (Samardakiewicz et al., 2012; Pirsellova et al., 2012). In a study in tomato, higher concentrations of Pb in the roots are also reported compared to the other products (Akinci, Akinci & Yilmaz, 2010).

In most plants, about 90% of total Pb accumulates in the root (Kumar et al. 1995) and the cell walls can immobilize Pb ions (Inoue et al. 2013). In the present study, roots accumulated 87.6% of Pb from the plant and 12.4% of Pb was translocated to the aerial part of the grasses.

The roots of high Andean grasslands tolerate and accumulate high levels of Pb and the highest overall rate of Pb accumulation occurred in the roots rather than in the shoots (Nascimento et al. 2014), suggesting that, under conditions of chronic contamination, it is a survival mechanism of the Andean pastures studied.

Lead concentration in shoots

In the study area, the pastures consumed by cattle showed a bioaccumulation of Pb above the permissible limits, which could generate problems of biomagnification in the food chains, damaging animal and human health and productivity (Chirinos-Peinado and Castro-Bedriñana, 2020). The average Pb content in shoots was 1.97 times higher than the limit value of 10 mg / kg for forages ($P < 0.01$) (Boularbah et al., 2006; Kabata-Pendias & Mukherjee, 2007) and 6.57 times higher than the critical value proposed for vegetables 0.05-3.0 mg / kg (Tokalioglu, Kartal & Gunis, 2000).

Normal Pb concentrations in mature leaf tissues of various plant species are between 5 and 10 mg / kg, considering a toxic range of 30 to 300 mg / kg (Kabata-Pendias & Mukherjee, 2007). Other proposals for an upper limit of Pb in pastures suggest 30 mg / kg of dry matter (Mlay and Mgumia, 2010; Adamse et al., 2017); however, this concentration in the long term may slow down plant growth and affect their biochemical functions (Sharma and Dubey, 2005); other authors propose as "normal level" values between 2 and 5 mg / kg (Robinson et al, 2008); even the Codex Alimentarius (ONU/FAO, 2018) indicates a maximum permissible limit of Pb in cattle feed of 0.3 mg / kg. The rules and regulations are increasingly strict, so recently the CDC, in only 8 years, has reduced the critical level of Pb in infants, from 10 to 2 ug/dL of blood (Rădulescu & Lundgren, 2019).

In the current study, no differences were found between Pb concentrations in natural and cultivated pastures, but they are higher than those reported in other regions of the country and the world (Longhurst, Roberts and Waller, 2004; Johnsen and Aaneby, 2019); they are higher than

the recommended guidelines for human health due to the risk of bioaccumulation in livestock products (Chirinos-Peinado and Castro-Bedriñana 2020).

The current results are slightly higher than those found in 31 species of *Brachiaria* in places around the refineries, with values between 9.8 and 16.0 mg / kg; in places around the exploration wells the values were between 9.7 and 13.2 mg / kg, with the highest concentrations recorded near the source of emission (Pelaez-Pelaez, Bustamante & Gomez, 2016).

In soils contaminated with Pb slag, levels of 209-899 (425 ± 79.0) mg / kg are reported, while in the control areas the average was 1.24 mg / kg (Ogundiran et al., 2012). In sites close to metallurgical activities, the Pb in forage was 29.06 ± 11.32 mg / kg (Swarup et al., 2005) while, in non-industrialized sites, the average was 2.08 ± 0.22 mg / kg. In this study, the average (19.71 ± 2.81 mg / kg) is attributed to sustained contamination from mining-metallurgical activity in the central sierra of Peru, constituting a permanent threat to Andean livestock (Iqbal et al., 2015).

In contaminated soils where there is cultivated pasture composed of *Trifolium alexandrinum*, *Brassica campestris* and *Avena sativa*, average Pb concentrations between 36.85 and 60.21 mg / kg are reported (Iqbal et al., 2015), higher values than those found in this study. In New Zealand's pastures, values between 4.4 and 26.8 mg / g (average 10.6 mg / kg) are reported (Martin et al., 2017) and between 6 and 16 mg / kg, depending on soil type (Longhurst, Roberts and Waller et al., 2004).

In practice, higher concentrations of Pb in forage roots are desirable so that grass shoots can be used as animal feed; however, the Pb levels determined in this study indicate that caution should be exercised when feeding animals with these grasses because they exceeded the 10 mg/kg forage threshold (Boularbah et al., 2006; Kabata-Pendias and Pendias, 2001).

Lead transfer in the soil root and bioaccumulation in the shoots

The Pb content of the soil is transferred and bioaccumulates in the edible parts of the forage, being a direct route for its incorporation into the food chain, causing damage to soil microorganisms, plants, animals and humans (Harmanescu et al., 2011; Alloway, 2013; Chirinos-Peinado and Castro-Bedriñana, 2020).

Under high contamination conditions, the transfer factor (TF) from soil to plant roots averaged 0.74 ± 0.26 (range: 0.54-0.94), a result that would show that the root absorbs and bioaccumulates a large part of the Pb present in the soil and retains it, transferring it to a lesser extent to the aerial part of the plant; however, the shoots had a high Pb content.

The determination of the BF of the heavy metals in the shoots in relation to the total soil content is a suitable method to quantify the bioavailability of the metals. Pb has a lower BF than other metals, as it is bound to the soil colloids, being less bioavailable (Violante et al., 2010). The BF of Pb from the soil colloids was slightly above the range of values of 0.01 to 0.10 for soils with 45 to 90 mg/kg Pb (Kloke, Sauerbeck and Vetter, 1984). In our case, the mean soil Pb content was 212.36 mg/kg and the BF range was 0.08 to 0.12; a result that indicates that the

highest proportion of Pb in natural and cultivated grasses remains concentrated in the root (Zhang et al., 2013; Song et al., 2019).

The BF in our study was below the average recorded for spinach, lettuce, carrots and radishes grown on soils containing 100 mg/kg Pb (Intawongse & Dean, 2008).

Our study shows that the mining and metallurgical activities carried out in the central highlands of Peru for almost a century have led to serious problems of environmental contamination in the root and pasture system of the soil used for cattle ranching in the central Andes of Peru; therefore, this is a critical problem that must be resolved (Akhtar et al., 2015; Nas and Ali, 2018).

Implications for central Peru

Our findings are important and impressive and demonstrate that the grasslands in the central highlands of Peru would have high concentrations of heavy metals compared to other parts of the country and the world, and could lead to undesirable economic and social outcomes, and regulations should be put in place to mitigate and correct this problem.

The data of this study evidence the agro-food production in substrates contaminated by Pb in the areas near the mining-metallurgical industry and if these activities do not improve their technological processes and implement strict environmental adaptation programs, the chronic bioaccumulation rate of Pb could continue with serious effects on environmental and human health, causing damage to the economic systems that affect the exposed populations. A new Peruvian guideline for Pb and other heavy metals levels in soil, forage and food could help to minimize the adverse effects of contamination.

Conclusions

The mining-metallurgical activity developed in central Peru during almost a century has had an impact on the high concentration of Pb in the upper soil layer and in natural and cultivated pastures of the Peruvian Andes. The average concentrations of lead in the soil, roots and shoots exceeded the maximum limits of international regulations. Lead in soil was 3.4 times higher than the maximum limit for agricultural soil and in forage was 1.97 times higher than the limit value for forage.

The study provides comparable information on the Pb content in the soil-root-plant system of pastures used to feed livestock raised in areas near polymetallic mining-metallurgical activity in the high central Andes of Peru.

This study is one of the first to evaluate the content and transfer of Pb in the soil-root-plant system in highly contaminated pastures, and the findings are shocking and could lead to socio-economic problems in exposed populations.

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Table 1(on next page)

Average and range of pH, organic matter (OM) and Pb content in the soil in different study periods in an area near the polymetallic smelter in the central Andean region of Peru.

Table 1. Average and range of pH, organic matter (OM) and Pb content in the soil in different study periods in an area near the polymetallic smelter in the central Andean region of Peru.

Period	pH	OM (%)	Pb (mg/kg)
Dry	6.34 [5.03-7.47]	3.89 [3.15-4.57]	206.91 [125.18-269.93]
Rain	6.38 [5.08-7.73]	3.93 [3.11-4.53]	217.81 [131.76-284.13]
Average	6.36 [5.03-7.73]	3.91 [3.11-4.57]	212.36 [125.18-284.13]

There are no statistical differences between average values per period ($P > 0.05$)

Table 2(on next page)

Lead concentration in soil, roots and shoots of high Andean pastures (mg / kg) in an area near the polymetallic smelter in the central Andean region of Peru.

Table 2. Lead concentration in soil, roots and shoots of high Andean pastures (mg / kg) in an area near the polymetallic smelter in the central Andean region of Peru.

	Natural pasture ¹		Cultivated pasture ²		All pastures	
	Average	95% CI	Average	95% CI	Average	95% CI
Soil	219.12	201.41-236.77	205.60	187.95-223.24	212.36a	200.08-224.64
Root	147.71	125.35-170.06	161.60	139.25-183.96	154.65b	137.75-171.56
Shoot	20.21	18.92-21.49	19.21	17.92-20.49	19.71c	18.81-20.60

a, b, c Average Pb contents: soil > root > shoot, vary statistically ($P < 0.01$)

¹ Natural grass composed of *Festuca dolichophylla*, *Piptochaetium faetertonei*, *Bromus catharticus*, *Bromus lanatus*, *Calamagrostis heterophylla*, *Nasella meyeniana*, *Nasella publiflora*, *Asiachnae pulvinata*, *Margaricarpus pinnatus*, *Oenothera multicaulis* y *Trifolium amabile*.

² Asociated pasture composed of *Lolium perenne* and *Trifoliums repens*.

Table 3(on next page)

Lead transfer factors in the soil-root-sprout system in high Andean pastures in an area near the polymetallic smelter in the central Andean region of Peru.

Table 3. Lead transfer factors in the soil-root-sprout system in high Andean pastures in an area near the polymetallic smelter in the central Andean region of Peru.

	Natural pasture ¹		Cultivated pasture ²		All pastures	
	Average	95% CI	Average	95% CI	Average	95% CI
Soil-root	0.68	0.57-0.79	0.81	0.69-0.92	0.74a	0.66-0.83
Root-shoot	0.15	0.13-0.18	0.14	0.11-0.16	0.14b	0.12-0.16
Soil-shoot	0.10	0.08-0.11	0.10	0.09-0.11	0.10c	0.09-0.11

a, b, c, Average Pb Transfer Factor: soil-root > root-shoot > soil-shoot ($P < 0.01$).

¹ Natural grass composed of *Festuca dolichophylla*, *Piptochaetium faetertonei*, *Bromus catharticus*, *Bromus lanatus*, *Calamagrostis heterophylla*, *Nasella meyeniana*, *Nasella publiflora*, *Asiachnae pulvinata*, *Margaricarpus pinnatus*, *Oenothera multicaulis* y *Trifolium amabile*.

² Asociated pasture composed of *Lolium perenne* and *Trifolium repens*.

Figure 1

Partial map of La Oroya-Peru, research area (3900-4500 m altitude). The image above shows the path from La Oroya Mining-Metallurgical complex.

The lower image shows the study site and distribution of sampling points (1 m²/sample).
Communal stable: to 20 km from La Oroya City. Sampling area (n = 10) of pastures cultivated - April samples Sampling area (n = 10) of pastures cultivated - September samples
Sampling area (n = 10) of natural pastures - April samples Sampling area (n = 10) of natural pastures - September samples



Figure 2

Average lead concentration in soil, roots and shoots from high Andean pastures in an area near the polymetallic smelter in the central Andean region of Peru.

The maximum permissible values of Pb in soil and grass are shown (MEF 2007; Kabata-Pendias & Pendias, 2001; Boularbah et al., 2006).

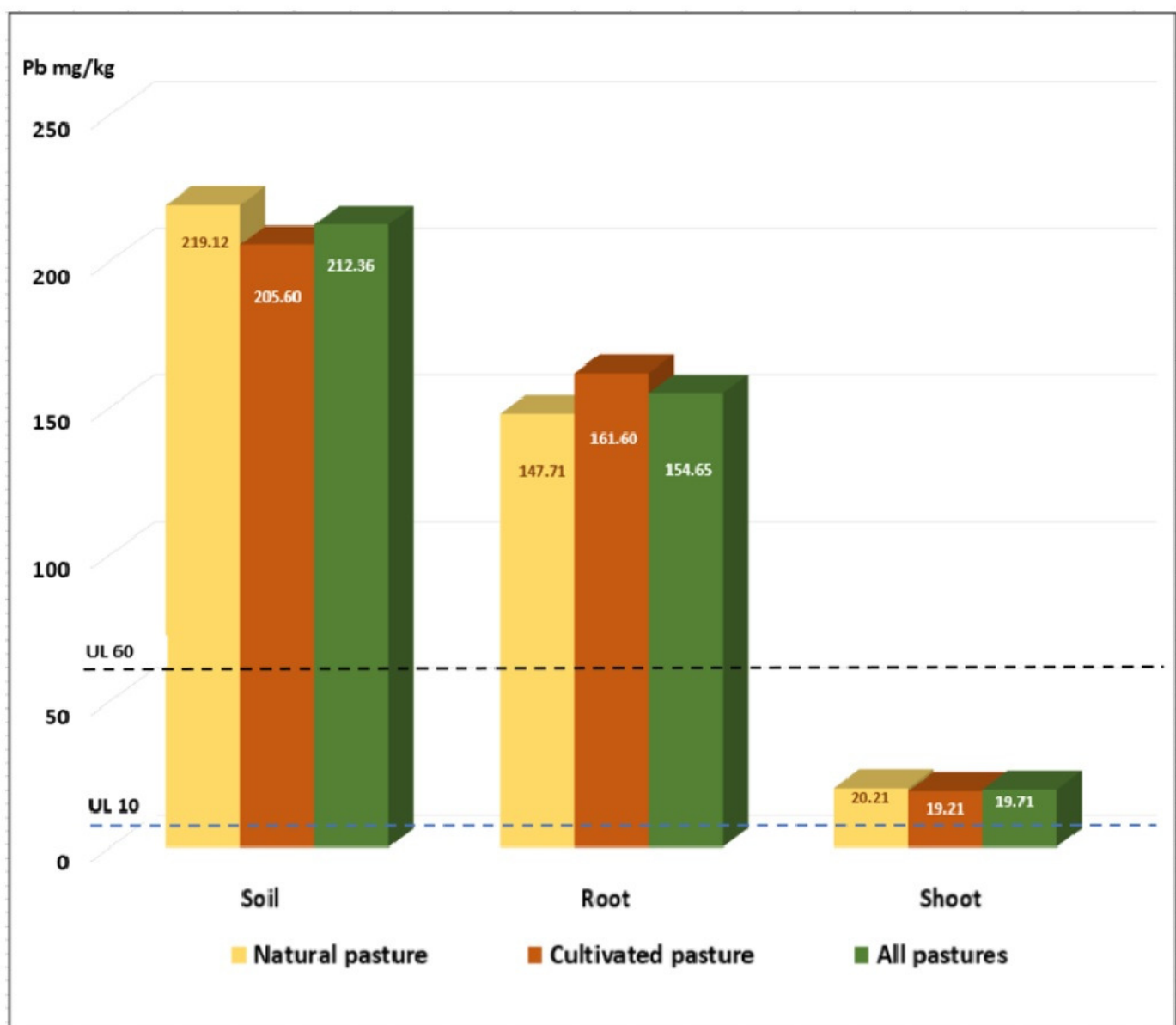


Figure 3

Lead transfer factors in soil-root-shoots system from natural and cultivated pastures in an area near the polymetallic smelter in the central Andean region of Peru.

